

## VOLATILIZATION OF SELENIUM FROM PLANTS AND SOILS

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### ABSTRACT

Volatilization of selenium was demonstrated with the two agronomic plant species, *Agrostis tenuis* Sibth. and *Hordeum vulgare* L. c.v. tyra grown in sealed chambers and rooted in soil or hydroponic solutions containing low concentrations of [ $^{75}\text{Se}$ ]-selenite. Volatile  $^{75}\text{Se}$  was recorded in the atmosphere surrounding the plants within 10 h after application of [ $^{75}\text{Se}$ ]-selenite to the growth medium, which coincided with the transport of selenium to the leaves.

In greenhouse experiments [ $^{75}\text{Se}$ ]-selenite spiked soil supporting barley plants evolved more selenium than the soil alone, again indicating that plants as well as soil micro-organisms play an important part in the process of selenium volatilization.

These results are discussed in relation to the atmospheric concentration of selenium throughout the year and the selenium concentrations in rain water.

### INTRODUCTION

The microbial formation of volatile selenium compounds, principally dimethylselenide, is widespread. Inorganic selenium, as well as organic selenium added to soil as plant and animal residues, may be converted to this volatile metabolite (Peterson, 1980; Doran, 1982).

As the evolution of volatile selenium from soils, sediments and sewage is a biological process, it is greatly influenced by the soil chemical and physical conditions including availability of selenium, carbon supply, temperature and water content as well as microbiological parameters. No volatilization occurs when soils are steam sterilized and microbiological activity eliminated (Chau et al., 1976; Zieve and Peterson, 1981; Reamer and Zoller, 1980). The evolution of volatile selenium from soils has been shown to be directly related to the content of water-soluble selenium (Abu-Erreish et al., 1968; Zieve and Peterson, 1981).

The release of volatile selenium from intact plants was first demonstrated by Lewis et al. (1966) working especially with accumulator plants, but the relevance of the experiments to field situations was not examined. Moreover,

this loss of selenium is usually associated with metabolism of high concentrations of selenium (Allaway, 1973).

As plant roots would compete with soil micro-organisms for available water-soluble selenium, it is of importance to establish whether volatile selenium compounds are given off from both components of the soil-plant system, and to determine the contributions each make to the total volatilization process. This paper reports the results from such experiments.

## MATERIALS AND METHODS

### *Measurement of selenium volatilization from plants — laboratory experiments*

Seeds were germinated on filter paper at 20°C and well established seedlings transferred to a modified Arnon and Hoagland solution (Peterson, 1969).

Plants were transferred to perspex chambers (22 × 20 × 25 cm) consisting of foliage and root compartments separated by a small compartment (1.5 cm) to avoid inadvertent leakage between compartments. The upper and the middle compartments had gas inlets and outlets.

Plants were inserted into the holes in the dividing base of the upper compartment, so that the roots were immersed in the nutrient solution and the shoots were contained in the upper compartment. The roots were sealed off from the upper chamber using silastic 738 RTV (Dow Corning, Brussels, Belgium) placed around the part of the stem passing through the holes. 10  $\mu\text{Ci}$  of  $^{75}\text{Se}$  (The Radiochemical Centre, Amersham) as sodium selenite containing 7  $\mu\text{g}$  of selenium  $\text{l}^{-1}$  were added to the growth medium. Air was passed through the chambers twice daily for 2 h at the rate of 15  $\text{ml min}^{-1}$  and the outgoing air was bubbled through 10 ml concentrated nitric acid traps. These traps, designed to fit a well-crystal scintillation counter, were assayed daily for radioactivity.

### *Measurement of selenium volatilization from plants — greenhouse experiments*

To measure the evolution of  $^{75}\text{Se}$  from soil, and soil plus barley plants, modified glass desiccators were used. Seeds were germinated for 3 days, and the seedlings transferred to the experimental system before addition of the isotope. The type of soil and the ratios of soil to water and  $^{75}\text{Se}$  isotope were the same as described previously (Zieve and Peterson, 1981). Each desiccator (13.5 cm in diameter) contained 400 g of air-dried soil that passed through 2 mm sieve. 40  $\mu\text{Ci}$  of  $^{75}\text{Se}$  (The Radiochemical Centre, Amersham) as sodium selenite containing 40  $\mu\text{g}$  of selenium in 56 ml water were added to the soil in each replicate desiccator. Thus 0.1 ppm selenium was added to a soil containing 5 ppm total selenium.

An outlet and an inlet gas line was inserted through the tap in each desiccator lid and the system operated in the same way as described earlier using

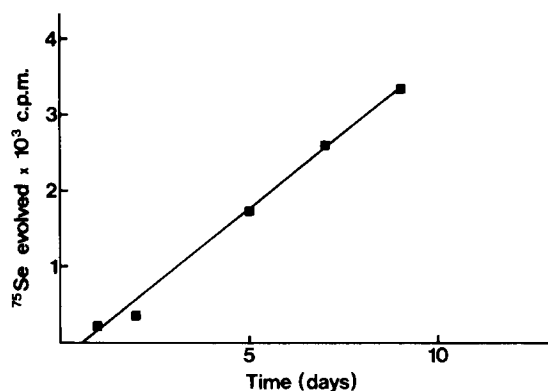


Fig. 1. Volatilization of [ $^{75}\text{Se}$ ]-selenium from leaves of *Agrostis tenuis* seedlings contained in an enclosed chamber and grown in a nutrient solution spiked with [ $^{75}\text{Se}$ ]-selenite.

nitric acid traps (Zieve and Peterson, 1981). Air was flushed through the desiccators twice daily for two hours at the rate of  $20 \text{ ml min}^{-1}$ .

## RESULTS AND DISCUSSION

Two species of plants were used in the study, one week old barley plants and six weeks old *Agrostis tenuis* (New Zealand). With both species, evolution of a volatile selenium compound commenced soon after the application of  $^{75}\text{Se}$  to the nutrient solution (Fig. 1 and 2), and much radioactivity could be detected within the first 24 h. As very low levels of selenium ( $7 \mu\text{g l}^{-1}$ ) were supplied to the nutrient solution these results show that selenium volatilization occurs from plants growing at selenium concentrations that can be found naturally in many soil solutions.

Figure 2 illustrates the relationship between Se accumulation in root and shoots and the evolution of  $^{75}\text{Se}$  to the atmosphere. The initial rapid increase in root selenium accumulation was considered to be mainly due to ion exchange processes, whilst the slower rise may be interpreted as an uptake component.

The volatilization of selenium as is evident from Fig. 2 is related to the rate of accumulation of the element. Volatiles were recorded in the atmosphere only 10 h after application of [ $^{75}\text{Se}$ ]-selenite to the nutrient solution, which coincided with the build-up of appreciable concentrations of selenium in the shoots.

Figure 3 shows the results of the greenhouse studies. It is evident that soil plus barley seedlings evolved more selenium than soil alone, reinforcing the view that plants also play a significant part in the volatilization process. However, the greenhouse experiment suggests that soil is the main source of volatile selenium although plants may increase the amount by about 15%.

The percentage of selenium volatilized from soil alone (0.14% after 18 days) was comparable in these experiments to the laboratory based studies reported earlier (Zieve and Peterson, 1981).

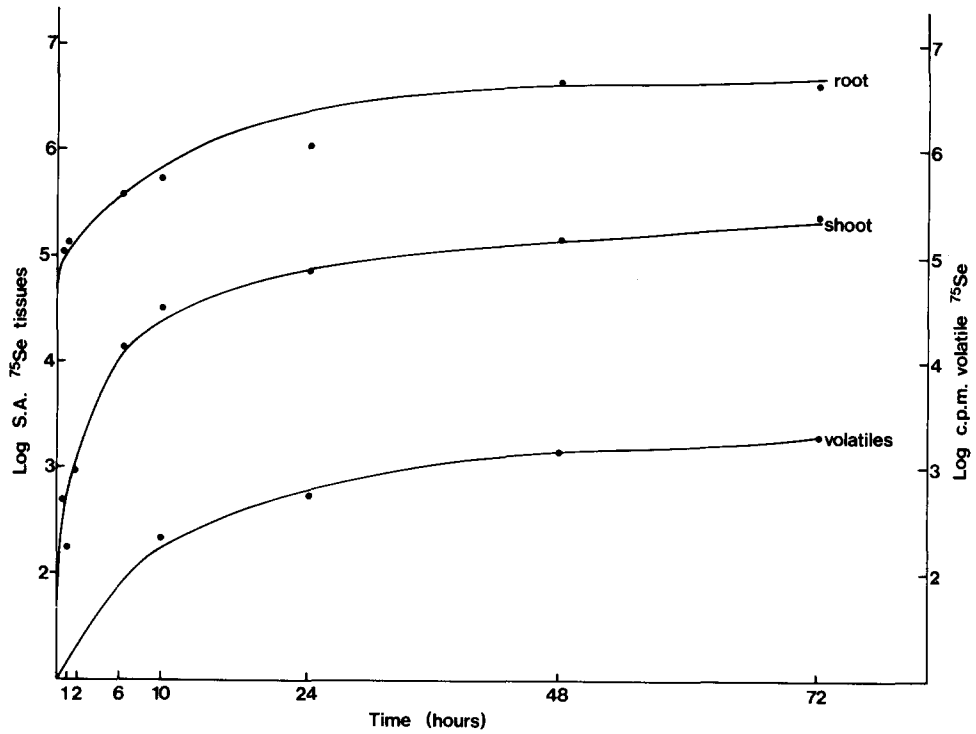


Fig. 2. Evolution of [ $^{75}\text{Se}$ ]-selenium from leaves of barley seedlings grown in enclosed chamber, in relation to shoot and root uptake.

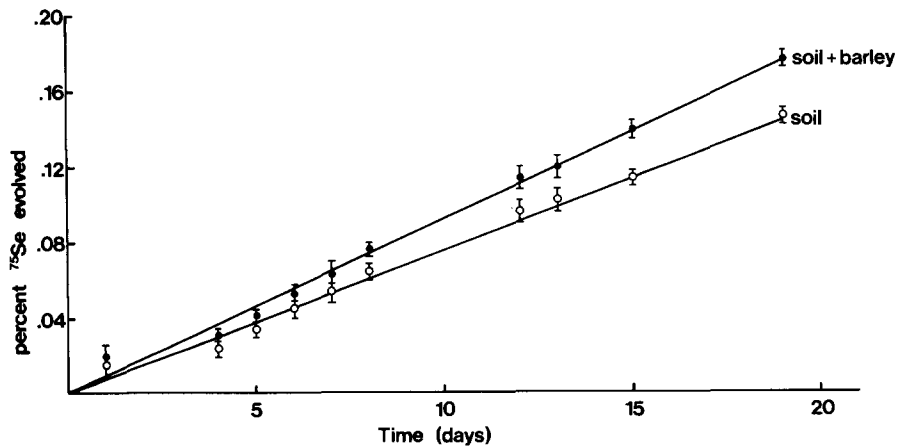


Fig. 3. Evolution of [ $^{75}\text{Se}$ ]-selenium from soil and soil + barley seedlings grown in desiccators under greenhouse conditions.

Barley and *Agrostis tenuis* seedlings were shown to be capable of metabolising inorganic selenium to volatile organic compounds within a relatively short period. These selenium volatiles are gaseous compounds compared with trace metals such as zinc and cadmium which may be released to the atmosphere as particulates from plant surfaces. Beauford and Barber (1975, 1977) studied the release of metals from the surface of *Pisum sativa* and *Pinus sylvestris* seedlings and suggested that as much as  $9 \text{ kg Zn km}^{-2}$  vegetation per year may be released to the atmosphere in particulate forms. This figure alone can give rise to as much as 36% of the total emission flux for this element (Lantzy and Mackenzie, 1979).

The experiments described here are not sufficient to assess the relative contribution of soil microorganisms and plants to atmospheric selenium as both organisms will compete to varying degrees for the same available selenium in the soil. Many plant factors such as species, age, size, growth rate etc. and various soil and climate factors will influence the magnitude of release of selenium to the atmosphere from the two components of the ecosystem.

Investigations into the sources of atmospheric selenium have indicated that much of this selenium is produced by natural processes (Duce et al., 1975; Weiss et al., 1971; Låg and Steinnes, 1978). Increased biological activity with rising temperatures during the spring may therefore explain the findings of McDonald and Duncan (1979) when they recorded higher levels of atmospheric selenium in the spring when compared with autumn or winter. This contrasts with many other elements including those of anthropogenic origin where the atmospheric levels were generally higher in the winter when combustion of fossil fuel is greatest. Furthermore, the contents of selenium in rainfall collected at six locations in Denmark was found to be higher for samples taken during spring and summer than in autumn or winter (Kubota et al., 1975).

A study of selenium and sulphur in Greenland ice cores showed that the sulphur content of the ice has increased in recent decades but that the selenium content has remained relatively constant (Weiss et al., 1971). The increase in the sulphur concentration has been attributed to fossil fuel burning. If this is true, then the lack of a selenium increase suggests that any selenium injected into the atmosphere during the burning of fossil fuels, is not being transported long distances in the atmosphere.

Thus the selenium concentrations found in the atmosphere in rural areas are probably the result of the emission of volatile selenium compounds from natural sources including volcanism.

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